Unique CO Chemisorption Properties of Gold Hexamer: $\text{Au}_6(\text{CO})_n^- (n = 0 - 3)$

Hua-Jin Zhai,† Boggavarapu Kiran,† Bing Dai,† Jun Li,‡ and Lai-Sheng Wang* †

Contribution from the Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99352, and W. R. Wiley Environmental Molecular Sciences Laboratory and Chemical Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352

Received April 21, 2005; E-mail: ls.wang@pnl.gov

Abstract: Elucidating the chemisorption properties of CO on gold clusters is essential to understanding the catalytic mechanisms of gold nanoparticles. Gold hexamer $\text{Au}_6$ is a highly stable cluster, known to possess a $D_{3h}$ triangular ground state structure with an extremely large HOMO–LUMO gap. Here we report a photoelectron spectroscopy (PES) and quasi-relativistic density functional theory (DFT) study of $\text{Au}_6\text{–CO}$ complexes, $\text{Au}_6(\text{CO})_n^-$ and $\text{Au}_6(\text{CO})_n^0 (n = 0 - 3)$. CO chemisorption on $\text{Au}_6$ is observed to be highly unusual. While the electron donor capability of CO is known to decrease the electron binding energies of $\text{Au}_6(\text{CO})_n^-$ complexes, CO chemisorption on $\text{Au}_6$ is observed to have very little effect on the electron binding energies of the first PES band of $\text{Au}_6(\text{CO})_n^- (n = 1 - 3)$. Extensive DFT calculations show that the first three CO successively chemisorb to the three apex sites of the $D_{3h} \text{Au}_6$. It is shown that the LUMO of the $\text{Au}_6\text{–CO}$ complexes is located in the inner triangle. Thus CO chemisorption on the apex sites (outer triangle) has little effect on this orbital, resulting in the roughly constant electron binding energies for the first PES band of $\text{Au}_6(\text{CO})_n^- (n = 0 - 3)$. Detailed molecular orbital analyses lead to decisive information about chemisorption interactions between CO and a model Au cluster.

1. Introduction

The discovery of remarkable catalytic activities of highly dispersed gold nanoparticles for low-temperature CO oxidation as pioneered by Haruta et al. has stimulated considerable research on gold clusters. Because of their potentials for industrial applications, extensive research efforts have been directed at elucidating the catalytic mechanisms of nanogold. Different models have been proposed, including the perimeter sites model, the nonmetallic gold model, the extra electron model, and the low-coordination sites model. However, the exact catalytic mechanisms are still being debated. Size-selected cluster deposition studies and gas-phase experimental and theoretical studies have been focused on larger clusters.

† Washington State University and Pacific Northwest National Laboratory.
‡ Pacific Northwest National Laboratory.

been carried out to model this catalytic reaction in a well-controlled manner, providing fundamental mechanistic information at the molecular level. Chemisorbed gold cluster complexes serve as ideal model systems for nanogold catalysts, even though the role of substrates cannot be addressed. Numerous mass spectrometric, photoelectron spectroscopic, and density functional theory (DFT) studies have established that O$_2$ adsorbs on gold clusters molecularly. Evidence for molecular chemisorption of O$_2$ on TiO$_2$-supported gold nanoparticles has also been observed recently. 5 Coadsorption of CO and O$_2$ on small gold clusters has been investigated by mass-spectrometry-based experiments, and it was revealed that CO and O$_2$ adsorb cooperatively, rather than competitively. 17,18

However, little experimental information is available on how CO molecules interact with gold clusters and gold nanoparticles. 19-23 Chemical reactions of gold clusters with CO have been studied, 19-22 and pronounced size dependence and saturation were observed. Infrared spectra of Au-CO complexes formed in a rare gas matrix have been reported, 23 and complexes such as Au(CO)$_n$ (n = 1–5) and Au$_2$(CO)$_2$ (n = 1, 2) were assigned. However, definitive electronic and structural information on the Au$_m$(CO)$_n$ complexes is still elusive. Such information would be valuable in the mechanistic understanding for the catalytic CO oxidation by gold nanoparticles.

In a recent communication, 22 we reported the generation of several series of gold carbonyl cluster anions Au$_m$(CO)$_n^-$ (m = 2–5, n = 1–7) in the gas phase and characterized their electronic structure using photoelectron spectroscopy (PES). We observed that the first few CO groups induce significant red shifts to the photoelectron spectra, suggesting that CO acts as electron donors to the gold clusters. For a given gold cluster, CO adsorption reaches a critical number, beyond which further CO adsorption changes the spectra very little. The critical CO numbers correspond exactly to the available low coordination sites only. Electronically, Au$_6$ is known to possess the largest HOMO–LUMO gap among gold clusters 34,35 and has been proposed to be a six-electron magic cluster within a two-dimensional electronic shell model. 39 Upon CO chemisorption, we observed surprisingly that the first three CO chemisorptions do not significantly change the electron binding energies of the first PES band in Au$_6$(CO)$_n^-$ (n = 1–3), in direct contrast to our previous study on the smaller Au$_n$(CO)$_m^-$(m = 2–5) complexes. Only the binding energies of the second PES band in Au$_6$(CO)$_n^-$ were observed to be red-shifted, resulting in a closing of the HOMO–LUMO gaps upon CO chemisorption. We also performed extensive quasi-relativistic DFT calculations to examine chemisorption structures in Au$_6$(CO)$_n^-$ and Au$_8$ (CO)$_n^-$ (n = 1–3). We found that the first three CO successively chemisorb to the apex sites of the triangular Au$_6$ without significantly perturbing the parent Au$_6$ structure. The unique CO chemisorption behavior and its influence on the electronic structure of Au$_6$ are understood using molecular orbital analysis, providing detailed information about the molecular and electronic interactions between CO and Au$_6$.

2. Experimental and Computational Methods

2.1. Photoelectron Spectroscopy

The experiments were carried out using a magnetic-bottle-type PES apparatus equipped with a laser vaporization supersonic cluster source, details of which were described elsewhere. 40 Briefly, Au$_m$(CO)$_n^-$ cluster anions were produced by laser vaporization of a pure gold target in the presence of a helium carrier gas seeded with 2% CO. Various Au$_m$(CO)$_n^-$ clusters were generated and mass-analyzed using a time-of-flight mass spectrometer. The Au$_m$(CO)$_n^-$ (n = 1–3) species were each mass-selected and decelerated before being photodetached. Three detachment photon energies were used in the current study: 532 nm (2.331 eV), 266 nm (4.661 eV), and 193 nm (6.424 eV). PES spectra were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. The PES spectra were calibrated using the known spectra of Au$^+$ and Rh$^+$, and the energy resolution of the apparatus was $\Delta E_d / E_d \sim 2.5\%$, that is, $\sim$25 meV for 1 eV electrons.

3. Results and Discussion

3.1. CO Chemisorption Behavior

In the current paper, we report a combined PES and DFT investigation of the CO chemisorption behavior on the gold hexamer from one to three CO groups, Au$_6$(CO)$_n^-$(n = 0–3). Bare gold hexamer has unique electronic and structural properties. 33–36 Structurally, Au$_6$ and Au$_6^-$ were well-characterized to possess a close-packed planar triangular structure with D$_{3h}$ symmetry. 36 This highly symmetric structure, stabilized by strong relativistic effects, 37 aromaticity, and aurophilic attraction, 38 may be viewed as a small piece of Au(111) surface or an ideal model catalytic surface composed of apex and edge sites only. Electronically, Au$_6$ is known to possess the largest HOMO–LUMO gap among gold clusters 34,35 and has been proposed to be a six-electron magic cluster within a two-dimensional electronic shell model. 39 Upon CO chemisorption, we observed surprisingly that the first three CO chemisorptions do not significantly change the electron binding energies of the first PES band in Au$_6$(CO)$_n^-$(n = 1–3), in direct contrast to our previous study on the smaller Au$_m$(CO)$_m^-$ (m = 2–5) complexes. Only the binding energies of the second PES band in Au$_6$(CO)$_n^-$ were observed to be red-shifted, resulting in a closing of the HOMO–LUMO gaps upon CO chemisorption.

The experiments were carried out in Au$_6$(CO)$_n^-$ and Au$_8$ (CO)$_n^-$ (n = 1–3). We found that the first three CO successively chemisorb to the apex sites of the triangular Au$_6$ without significantly perturbing the parent Au$_6$ structure. The unique CO chemisorption behavior and its influence on the electronic structure of Au$_6$ are understood using molecular orbital analysis, providing detailed information about the molecular and electronic interactions between CO and Au$_6$.
2.2. Density Functional Calculations. In the DFT calculations, we used the Stuttgart 19-valence-electron energy-consistent pseudopotentials and basis sets augmented with two f-type and one g-type polarization functions ($\zeta_f = 0.498, 1.461$, and $\zeta_g = 1.218$) for gold as recommended by Martin and Sundermann and Dunning’s all-electron basis set aug-cc-pVTZ for oxygen and carbon. Scalar (mass-velocity and Darwin) relativistic effects were taken into account via the quasi-relativistic pseudopotentials. A variety of exchange-correlation functionals were tested for accuracy and consistency. We found that the B3LYP hybrid functional, which makes use of the Hartree–Fock exact exchange and Becke’s exchange functional and Lee–Yang–Parr correlation functional, gave electron binding energies in good agreement with the experimental data. Harmonic frequency calculations were performed to verify that the obtained structures are minima on the potential energy surfaces. All calculations were spin-restricted for closed-shell molecules and spin-unrestricted for open-shell species. Adiabatic detachment energies (ADEs) were calculated via the total energy difference (i.e., $\Delta SCF$ method), whereas the vertical detachment energies (VDEs) for the anionic clusters were calculated using the combined $\Delta SCF$-TDDFT approach. For all calculations, the extra fine integration grid was used to obtain highly accurate DFT results. All calculations were accomplished using the NWChem 4.6 program and the Molecular Science Computing Facility located at the Environmental Molecular Sciences Laboratory. Molecular orbitals were visualized using GaussView 3.0.

3. Experimental Results

The PES spectra of Au$_6$(CO)$_n^-$ ($n = 0–3$) were obtained at three detachment photon energies (532, 266, and 193 nm). Figure 1 compares the 193 nm spectra of all the species. The spectra at all three photon energies are given as Supporting Information in Figures S1–S4. The lower photon energy spectra had better spectral resolution and yielded more accurate ADEs and VDEs, which are summarized in Table 1 for the first two detachment features (bands X and A in Figure 1). Since no vibrational structures were resolved in the PES data, the ADEs, that is, the electron affinities of the corresponding neutral clusters, were evaluated by drawing a straight line at the leading edge of the ground-state feature X and then adding the instrumental resolution to the intersections with the binding energy axis. Although this is an approximate procedure, we were able to obtain consistent ADEs from spectra taken at different photon energies due to the relatively sharp onset of the data. The VDE differences between bands A and X give approximately the experimental measures for the HOMO–LUMO gap of the neutral complexes and are given in Table 2. The VDE and ADE difference of band X defines the reorganization energy (Table 2), which is a measure of the geometry changes between the anion and neutral ground states. The VDEs for all

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Well-resolved PES spectra for Au$_6$ were presented in our previous work. The ADE and VDE of the ground-state X were measured to be 2.06 and 2.13 eV, respectively, where the ADE is in good agreement with a previous ZEKE measurement (2.05 eV). The VDE of band A at 4.43 eV defines an extremely large HOMO-LUMO gap of 2.30 eV for neutral Au$_6$, which is the largest among all gold clusters. Upon adsorption of the first CO, the ground state feature X broadened (Figure 1b), but its binding energies (ADE: 2.04 eV; VDE: 2.20 eV) showed very little change relative to that of the bare cluster. This is completely different from the chemisorption behavior of the smaller gold clusters, where a red shift of as much as 0.6 to 0.7 eV was observed upon the first CO chemisorption for Au$_n$ ($n = 2-5$). However, the second VDE, corresponding to electron detachment from the anion ground state to the first neutral excited state (A), was measured to be 3.92 eV, significantly red-shifted by 0.51 eV with respect to that of Au$_6$ and resulting in a much smaller X-A energy gap (1.72 eV).

Upon further CO adsorption, the overall spectral patterns of Au$_6$(CO)$_n$ and Au$_6$(CO)$_n^-$ ($n = 0-3$) appeared similar to that of Au$_6$(CO)$_2^-$: the first PES band X showed very little dependence on the number of CO ligands, whereas the higher binding energy features displayed continued red shifts, resulting in smaller and smaller X-A energy gaps: 1.45 eV for Au$_6$(CO)$_2^-$ and 1.17 eV for Au$_6$(CO)$_3^-$. Very weak signals were observed in the X-A gap region in the spectra of the CO chemisorbed species (Figure 1). These weak signals were likely due to minor structural isomers in the CO-chemisorbed complexes. Stronger signals were observed in the X-A gap region in the chemisorbed species at 266 nm (Spectra S2–S4). In fact, weak signals were also present in the 266 nm spectrum of the bare Au$_6^-$(Figure S1b). These enhanced signals in the X-A gap region in the chemisorbed species at 266 nm were most likely due to autodetachment, which has been observed in other clusters with large HOMO-LUMO gaps, in particular for C$_{60}^-$ and Au$_{20}^-$.46,49

4. Computational Results

To find the CO chemisorption sites on the gold hexamer, we searched a variety of isomers for Au$_6$(CO)$_n$ and Au$_6$(CO)$_n^-$ ($n = 0-3$). Optimized ground state and selected low-lying isomers for Au$_6$(CO)$_n$ and Au$_6$(CO)$_n^-$ (1–18) are presented in Figures 2–4. Optimized structures for other isomers and their relative energies are presented as Supporting Information in Figures S5–S7. The computed ADEs for the ground state and computed VDEs for the ground and first excited states of the lowest energy isomers are compared with the experimental data in Table 1. The computed VDEs for all the detachment channels up to the 193 nm photon energy for the global minimum structures are given in Tables S1–S4. On the basis of these computed VDEs, we simulated the photoelectron spectra by convoluting each vertical detachment energy with a Gaussian function, as shown in Figure 5. In addition, the CO chemisorption energies were also computed, as compared with previous DFT results in Table 3. Since we were only concerned with the trend of the adsorption energies, no zero-point energy corrections and basis set superposition error (BSSE) corrections were pursued.


Figure 2. Optimized structures of the ground state and a low-lying isomer for Au$_6^-$, Au$_6$(CO)$^-$, and their corresponding neutrals. All bond lengths are in Å, and all relative energies (in eV) are referenced to the anion ground state.

Figure 3. Optimized structures of the ground state and a low-lying isomer for Au$_6$(CO)$_2^-$(1) and Au$_6$(CO)$_3^-$(2) appeared similar to that of Au$_6$(CO)$_2^-$: the first PES band X showed very little dependence on the number of CO ligands, whereas the higher binding energy features displayed continued red shifts, resulting in smaller and smaller X-A energy gaps: 1.45 eV for Au$_6$(CO)$_2^-$ and 1.17 eV for Au$_6$(CO)$_3^-$. Very weak signals were observed in the X-A gap region in the spectra of the CO chemisorbed species (Figure 1). These weak signals were likely due to minor structural isomers in the CO-chemisorbed complexes. Stronger signals were observed in the X-A gap region in the chemisorbed species at 266 nm (Spectra S2–S4). In fact, weak signals were also present in the 266 nm spectrum of the bare Au$_6^-$(Figure S1b). These enhanced signals in the X-A gap region in the chemisorbed species at 266 nm were most likely due to autodetachment, which has been observed in other clusters with large HOMO-LUMO gaps, in particular for C$_{60}^-$ and Au$_{20}^-$.46,49

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4.1. $\text{Au}_6^-$ and $\text{Au}_6$. The identified ground state (1) of $\text{Au}_6^-$ is $2A_1'$ with one electron occupying the 6s-derived antibonding $a_1'$ orbital of $D_{3h}$ symmetry, in agreement with numerous previous theoretical calculations. As shown in Figure 2, the structure (1) can be viewed as composed of an inner triangle made from the three edge atoms and an outer triangle made from the three apex atoms. The ground state of $\text{Au}_6$ ($3D_{3h}^1A_1'$) is similar to the anion with some minor geometrical changes. In the anion ground state (1), all $\text{Au}^-\text{Au}$ bond distances are almost equal, and the bond angle of the three edge atoms is almost linear ($\angle \text{Au}^-\text{Au}^-\text{Au} = 179.2^\circ$). Upon detachment of the extra electron, the inner triangle is slightly expanded while the outer triangle is slightly contracted because the extra electron is removed from the outer triangle. The anion-to-neutral structural changes from (1) to (3) can be understood from the LUMO of $\text{Au}_6^-$ or the singly occupied anion MO (SOMO $6a_1'$, Figure 6A), which is largely localized on the apex sites and exhibit weak bonding within the inner triangle and weak antibonding characters between the inner triangle and the apex atoms. We located a low-lying isomer for $\text{Au}_6^-$ ($2D_{3h} A_2^1$, Figure 2), which was found to be only 0.30 eV higher in energy. The corresponding neutral $D_{3h}$ structure (4) was found to be 1.70 eV higher in energy.

4.2. $\text{Au}_6(\text{CO})^-$ and $\text{Au}_6(\text{CO})$. The ground state and a low-lying isomer for $\text{Au}_6(\text{CO})^-$ and $\text{Au}_6(\text{CO})$ are also given in Figure 2. The anion ground state (5) is $3B_2$ with $C_{2v}$ symmetry, in which CO chemisorbs to an apex site of the triangular $\text{Au}_6^-$ cluster. The CO chemisorption results in a slight and interesting structural distortion in the $\text{Au}_6^-$ motif: the inner triangle is slightly expanded, and the overall shape of the $\text{Au}_6$ motif appears slightly elongated along the CO direction. A $C_{2v}$ ($3B_2$) isomer (6) of $\text{Au}_6(\text{CO})^-$, derived from the $D_{3h}$ isomer of $\text{Au}_6^-$, was found to be almost degenerate with the $C_{2v}$ ground state structure, only 0.03 eV higher in energy at the current level of theory. For neutral $\text{Au}_6(\text{CO})$, the triangular structure (7) was found to be the ground state, whereas the $C_{2v}$ isomer (8) was found to be substantially higher in energy (by 0.99 eV). Our calculated CO chemisorption energy is 0.69 eV in $\text{Au}_6(\text{CO})^-$ and 0.61 eV in the neutral complex (Table 3).

4.3. $\text{Au}_6(\text{CO})_2^-$ and $\text{Au}_6(\text{CO})_2$. The second CO also chemisorbs to an apex site on the triangular gold hexamer (Figure 3). The geometry of the $\text{Au}_6(\text{CO})_2^-$ ground state (9 $C_{2v} A_1^2$) is similar to that of $\text{Au}_6(\text{CO})^-$: the second CO appears to cause the two $\text{Au}^-\text{Au}$ bonds between the two chemisorption sites to lengthen. The only notable structural change between the ground state of $\text{Au}_6(\text{CO})_2^-$ and that of the neutral (11) is with respect...
structure related to the $C_2$ isomer of the anion was found to be a low-lying isomer for neutral Au$_6$(CO)$_2$ \textsuperscript{12}, which is 0.67 eV higher in energy than the triangular structure \textsuperscript{11}. But the structure of this Au$_6$(CO)$_2$ isomer is completely distorted, in which one Au–Au bond is broken, leading to the low symmetry $C_1$ ($^{1}A'$) structure \textsuperscript{12}. The chemisorption energy per CO in Au$_6$(CO)$_2^-$ and Au$_6$(CO)$_2$ decreases only slightly relative to the mono-CO chemisorbed systems (Table 3).

4.4. Au$_6$(CO)$_3^-$ and Au$_6$(CO)$_3$. Three anion structures \textsuperscript{13–15} were identified for Au$_6$(CO)$_3^-$, which are energetically degenerate at the B3LYP level and cannot be differentiated without accurate account of the dispersion electron correlation effects. Their corresponding neutral structures \textsuperscript{16–18} were also identified as minima. However, in the neutrals, the triangular Au$_6$-based structure $C_{3h}$ ($^{1}A'$) is clearly the ground state \textsuperscript{16}, with the $D_{3h}$ Au$_6$-based structures \textsuperscript{17 and 18} being 0.75 and 0.34 eV higher, respectively. Note that structures \textsuperscript{13 and 16} are significantly different in the CO chemisorption angles. Structure \textsuperscript{13} is derived from the ground-state structure of Au$_6$(CO)$_2^-$ \textsuperscript{9} by adsorbing a CO to the third apex site. In structure \textsuperscript{16}, CO is almost collinear with one of the edges of the triangular Au$_6$, forming a propeller shaped $C_{3h}$ structure. Structures \textsuperscript{14 and 15} are derived from the $D_{3h}$ isomers of Au$_6^-$ \textsuperscript{2} with CO adsorbed at different positions. The chemisorption energy per CO in the triangular Au$_6$(CO)$_3^-$ \textsuperscript{13} seemed to decrease slightly relative to that in Au$_6$(CO)$_2^-$, whereas in neutral Au$_6$(CO)$_3$, the per CO chemisorption energy is nearly the same as that in Au$_6$(CO)$_2$ (Table 3).

5. Discussion

5.1. Comparison between the Experimental Data and Theoretical Calculations. The calculated ADEs for the ground-state transitions, i.e., the electron affinities for neutral Au$_6$(CO)$_n$ ($n = 0–3$), are compared to the experimental values in Table 1. These values, computed from the differences between the total energies of the ground states of the anions and that of the neutrals, were all based on the triangular Au$_6$. Excellent agreement was observed between the calculated and experimental ADEs. For Au$_6$(CO)$_3^-$, there are three nearly degenerate structures competing for the ground state (Figure 4). However, only the triangular Au$_6$-derived structure \textsuperscript{13} yielded an ADE that agrees with the experiment. The ADEs calculated for the two structures derived from the $D_{2h}$ Au$_6$ isomer \textsuperscript{14, 15} were both much higher than the experimental value because the corresponding neutrals were found to be significantly higher in energy than the triangular structure (Figure 4). The calculated VDEs from the triangular Au$_6$ derived ground-state Au$_6$(CO)$_n^-$ ($n = 0–3$) are also in excellent agreement with the experiment (Table 1).

The computed reorganization energies are compared with the experimental values in Table 2. Excellent agreement was also observed. The relatively small values of the reorganization energies are consistent with the small geometrical changes between the anion and the neutral ground states from the triangular Au$_6$ derived complexes (Figures 2–4). The largest reorganization energy was for the three CO chemisorbed complex, largely due to the CO bond angle changes between the anion \textsuperscript{13} and the neutral \textsuperscript{16} (Figure 4).

The calculated VDEs for the first excited state of neutral Au$_6$(CO)$_n$ ($n = 0–3$) are also compared with the experimental

![Figure 5. Simulated photoelectron spectra for the ground-state structures of Au$_6$(CO)$_n^-$ ($n = 0–3$). The spectra were constructed by fitting the distribution of the calculated VDEs with unit-area Gaussian functions of 0.04 eV width.](image-url)
values in Table 1. The theoretical results are in perfect agreement with the experiment. The difference between the VDEs of the first excited state and of the ground-state detachment transitions defines the X−A energy gap, an approximate measure of the HOMO−LUMO gap of the neutral complexes. We see from Table 2 that the computed HOMO−LUMO gaps agree very well with the experimental values. In particular, the large HOMO−LUMO gap of Au6 was well reproduced, as well as the trend of the decreasing gaps in the Au6(CO)n complexes with increasing CO chemisorption.

The PES spectra beyond the first excited-state become much more complicated with a very high density of electronic states. We also computed VDEs for the higher detachment channels up to the 193 nm photon energy. Numerical values are given in Tables S1−S4 for Au6(CO)n− (n = 0−3), respectively. Simulated spectra based on the computed VDEs are shown in Figure 5. The simulated spectra agree qualitatively with the experimental spectra (Figure 1). As discussed above, the first two detachment transitions, as well as the trend of the energy gap, reproduced well the experimental observation. The weak signals observed in the HOMO−LUMO gap region in the experimental spectra of the chemisorbed complexes (Figure 1) were most likely due to the D2h Au6− derived isomers. The computed ADEs and VDEs for these isomers (Tables S2−S4) agree with the experimental observation.

5.2. Electronic Structure and Chemical Bonding in Au6. Before the discussion of the chemical interactions between Au6 and CO, it is instructive to examine the bare Au6 neutral. The bonding in Au6 can be understood by mainly considering the orbital interactions of the Au 6s1 electrons; the Au 5d10 manifold can be qualitatively viewed as being simply broadened upon orbital overlap. As shown in Figure 7, the 6s orbitals of the inner Au3(i) and outer Au3(o) triangles in Au6 both form a′ +
e' representations. The orbital interaction between the inner and outer Au3 fragments leads to the formation of a bonding and antibonding pair of $a_1' + e'$. The six 6s electrons fully occupy the $a_1' + e'$ bonding orbitals, giving rise to a $(a_1')^2(e')^4(a_1')^0$ electron configuration, which is analogous to the delocalized $\pi$ electrons in benzene. The antibonding $a_1' + e'$ orbitals, which are nearly degenerate, are unoccupied and become the LUMO and LUMO+1, respectively (Figure 7). This unique electron configuration and the delocalized nature of the $a_1' + e'$ orbitals render Au6 a highly $\sigma$-aromatic system, explaining its special stability and its extremely large HOMO-LUMO gap.

As shown in Figure 6A, the $a_1'$ LUMO of Au6 (the 6a1' SOMO in Au6-) is mainly from the outer Au3 fragment, whereas the $e'$ LUMO+1 orbitals (8e') are mainly from the inner Au3 fragment. The different spatial distributions of these orbitals and their near degeneracy turn out to be the key in understanding the interaction of Au6 and CO.

5.3. Electronic Structure Evolution and Chemical Bonding in Au6(CO)n−. As noted above, there are two major surprising experimental observations for CO interacting with Au6-. In contrast to the smaller gold clusters, chemisorptions of CO on Au6 do not alter significantly the electron binding energies in the Au6(CO)n− complexes, whereas the X−A band gap decreases continuously with increasing CO chemisorption (Figure 1). This indicates that the LUMO of the neutral Au6(CO)n complexes, into which the extra electron occupies in the anions, is energetically not affected by the CO chemisorption, while the HOMO is pushed up in energy. These observations can be understood from the above MO analysis for Au6 and the schematic MO level diagram depicted in Figure 8. The HOMO of Au6 is the degenerate 7e' orbitals (Figure 6A), which involve strong s−d hybridization and are highly delocalized. The LUMO of Au6 is 6a1' (Figure 6A), which is mainly distributed on the three apex atoms (outer triangle). In the Au6− anion the extra electron enters the 6a1' orbital and the charge is distributed on the outer triangle. What is unique to Au6 is that its LUMO+1 (8e') (Figure 6A), which is mainly concentrated on the inner triangle, is very close in energy to the LUMO, as shown in Figure 8. The consequence of this energetic proximity between the LUMO and LUMO+1 in Au6 will become clear when CO is adsorbed.

When one CO is coordinated to an apex atom of Au6, the symmetry of the molecule is lowered from $D_{3h}$ to $C_{2v}$, and the degenerate LUMO+1 (8e') of Au6 is split into $a_1$ and $b_2$ orbitals. The $a_1$ component of the 8e' orbital strongly mixes with the 6a1' orbital, which are both destabilized (Figure 8). On the other hand, the $b_2$ component of the 8e' orbital interacting with the CO 2\pi orbitals becomes the LUMO, into which the extra electron enters in Au6(CO)−. Consequently, the CO chemisorption to Au6− induces an internal electron transfer from the outer triangle to the inner triangle. Since the $b_2$ LUMO of Au6(CO)− (11b2) does not change much energetically relative to that in the bare Au6 species, similar electron binding energies are expected for the two systems. In Au6(CO)2− and Au6(CO)3−, the $a_1$ component of the 8e' orbital becomes the LUMO, which is again localized on the inner triangle (Figure 6) and whose binding energy is not expected to change significantly relative to that of Au6−. This situation is unique to the $D_{3h}$ Au6 structure, where there exist two spatially distinct but energetically similar regions in the molecule. Thus, in the anions, the extra electron shuttles from the outer triangle to the inner triangle upon chemisorption, resulting in a relatively constant electron binding energy for the SOMO in both Au6− and Au6(CO)n− ($n = 1−3$) (Figure 8). In other words, since the extra electron in Au6(CO)n− ($n = 1−3$) is localized on the inner Au atoms, it is not sensitive to the CO chemisorption, which only involves the outer Au atoms. This is also reflected in the similar CO binding energies between the Au6(CO)n− neutrals and the Au6(CO)n− anions and their relative independence of the CO numbers (Table 3).
The CO chemisorption also lifts the degeneracy of the 7e′ HOMO of the $D_{3h}$ Au$_6$, forming $a_1$ and $b_2$ orbitals under the $C_2v$ symmetry in Au$_6$(CO)$_n$. The $a_1$ or $b_2$ orbital from the HOMO mixes with the corresponding orbital from the LUMO, pushing up the HOMO level in the chemisorbed complexes, $15a_1$ for $n = 1$, $13b_2$ for $n = 2$, and $14b_2$ for $n = 3$ (Figure 8). The destabilization of the HOMO in the chemisorbed systems is further enhanced by the CO 5σ-donation, which is repulsive due to closed-shell/closed-shell interactions. The relatively constant LUMO level plus the destabilization of the HOMO level in Au$_6$(CO)$_n$ gives rise to the decreasing band gaps observed in the chemisorbed complexes.

The large HOMO–LUMO gap in Au$_6$ arises from the σ-aromaticity of the Au$_6$ 6s manifold. Accordingly, the Au$_6$ cluster is quite inert chemically, and it is known not to be reactive to O$_2$. The destabilization of its HOMO upon CO chemisorption provides an important activation mechanism. Thus it is expected that neutral chemisorbed Au$_6$(CO)$_n$ complexes should be reactive toward O$_2$. This cooperative chemisorption behavior seems to be an essential feature in considering the catalytic mechanisms of nanogold for CO oxidation.

6. Conclusions

We report a combined photoelectron spectroscopic and theoretical investigation of Au$_6$(CO)$_n$ (n = 0–3). Photoelectron spectra were obtained at several photon energies and revealed surprisingly that the electron affinities of Au$_6$(CO)$_n$ are relatively independent of the CO chemisorption, whereas the HOMO–LUMO gap decreases with CO chemisorption. Extensive density functional calculations were carried out, showing that CO prefers to bind to the apex sites of the triangular Au$_6$ in both Au$_6$(CO)$_n$ and Au$_6$(CO)$_n^-$ (n = 1–3). The experimental observation was elucidated through molecular orbital analyses, yielding detailed information about the molecular interactions between CO and Au$_6$. The unique triangular structure of Au$_6$ is responsible for the surprising experimental observation. It turns out that the LUMO (6a$_1'$) and LUMO+1 (8e′) of Au$_6$ are nearly degenerate and they are localized on the outer and inner Au$_3$ triangles of the $D_{3h}$ Au$_6$, respectively. Upon CO chemisorption, the symmetry of the chemisorbed complexes is lowered and the degeneracy of the LUMO+1 is lifted. One component of the LUMO+1 orbital in Au$_6$ becomes the LUMO in the Au$_6$(CO)$_n$ complexes. Since the LUMO in the Au$_6$(CO)$_n$ complexes is mainly localized in the inner triangle of the Au$_6$ substrate, it is not affected energetically by the CO chemisorption; i.e., an electron shuttling from the outer triangle to the inner triangle takes place upon CO chemisorption in the negatively charged systems. On the other hand, the HOMO of Au$_6$ is destabilized upon CO chemisorption due to both HOMO–LUMO orbital interactions and the CO 5σ-donation, causing the decreasing HOMO–LUMO gap. This series of complexes thus provides ideal molecular models of nanogold catalysts for CO oxidation. The destabilization of the HOMO of Au$_6$ upon CO chemisorption should promote reactions with O$_2$, providing a mechanism for cooperative chemisorption and catalytic reactions.

Acknowledgment. This work was supported by the National Science Foundation (CHE-0349426) and performed at the W. R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the Department of Energy’s Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory, operated for DOE by Battelle. All calculations were performed with supercomputers at the EMSL Molecular Science Computing Facility.

Supporting Information Available: The complete sets of photoelectron spectra for Au$_6$(CO)$_n^-$ (n = 0–3) at 532, 266, and 193 nm, experimental and theoretical electron detachment energies, and alternative structures optimized for the anions and neutrals along with their relative energies. This material is available free of charge via the Internet at http://pubs.acs.org.